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Heat effect of the oxygen-containing functional groups in coal during spontaneous combustion processes

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ABSTRACT

The heat generated from the reactions of oxygen-containing functional groups in coal has been studied using organic chemistry and quantum chemistry analysis methods. Structural models of the oxygen-containing functional groups in coal were established and used to analyze the reactions of these groups during spontaneous combustion. The Gibbs free energy and enthalpy changes associated with these reactions were determined using quantum mechanical analysis, and the results indicated that the dehydration and dehydrogenation reactions of the hydroxyl groups in coal were only mildly exothermic, whereas reactions involving the oxidation of the carbonyl groups were much more exothermic. In contrast, reactions resulting in the generation of carbon monoxide were endothermic. By comparing the heat release characteristics of the reactions of the oxygen-containing functional groups with the levels of oxygen consumption and gas production, as well as temperature profiles of the reactions, it was concluded that the decomposition of oxygen-containing functional groups is critical to the production of heat during the initial stages of the spontaneous combustion of coal and that oxidation does not occur during this period. These results also explain why the temperature of coal rises slowly during the initial stages of its spontaneous combustion.

1. Introduction

The spontaneous combustion of coal essentially involves the decomposition and oxidation reactions of the active functional groups within the coal [1–7], and the heat released from the reaction of active functional groups on the surface of the coal particles accumulates, leading to an increase in the temperature. Research towards the heat effects of the different active functional groups in coal is therefore critical to developing a deeper understanding the processes involved in the spontaneous combustion of coal.

Recent studies in this area have demonstrated that the main functional groups in coal are oxygen-containing functional groups, as well as aliphatic and aromatic hydrocarbons [8–14]. Aromatic hydrocarbons represent the core structure of coal, and these structural units are connected by aliphatic side chains and oxygen-containing functional groups [15–18]. The aromatic hydrocarbon groups in coal are more stable than the oxygen-containing functional groups and the aliphatic hydrocarbons, and do not react when the temperature of the coal is low. The aliphatic hydrocarbon groups are more active than the aromatic hydrocarbons because they posses reactive side chains [14]. Among all of the reactive functional groups present in coal, those containing oxygen are the most active and represent the main reactants during the spontaneous combustion of coal, where they have a significant impact on the nature of coal [19]. For this reason, significant research efforts have been focused on the distribution and structural characterization of the oxygen-containing functional groups involved in the spontaneous combustion of coal [1,2,13,20–26]. Despite extensive research in these areas, studies directed towards the heat effects of the different oxygen-containing functional groups have been scarce.

Several model systems of oxygen-containing functional groups were constructed in this study to determine the extent to which these groups contributed to the spontaneous combustion of coal. Equations describing the chemical reactions occurring in each model were subsequently analyzed according to their chemical characteristics, and chemical calculation methods were applied to determine the heat effects associated with each reaction. The results of these calculations were also compared with the temperature, oxygen consumption, and gas production characteristics during the self-heating process of coal. The results of this study will provide useful information concerning the effects of oxygen-containing functional groups on the spontaneous combustion of

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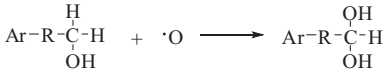
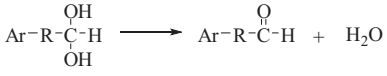
coal at low temperatures. These results could also be used to develop better materials to prevent the spontaneous combustion of coal.

2. Types and computational models of oxygen functional group

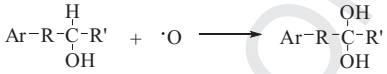
To develop a deeper understanding of the heat effects associated with the different oxygen-containing functional groups, we analyzed the chemical reaction processes of each type of oxygen-containing functional groups according to the processes described below, where Ar has been used to represent phenyl groups, and R and R' have been used to represent segments of the aliphatic structure of coal. The FTIR analysis of the raw coals revealed that the most active oxygen-containing functional groups were hydroxyl (—OH), carboxyl (—COOH), and carbonyl (—CH=O) groups [1,14].

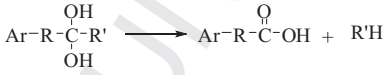
The —OH groups in coal always directly connect to aliphatic hydrocarbon. When a —OH group is located at the end of an aliphatic chain, oxygen initially combines with the carbon atom connected to the —OH group to form a second —OH group. The resulting dihydroxylated species can then undergo a dehydration reaction to give a —CH=O group (i.e., an aldehyde) [27]. This entire process can be described as follows.



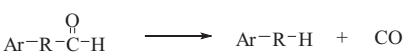


If the —OH group is connected to a carbon atom within an aliphatic carbon chain, then the carbon atom connected to the —OH can still react with oxygen to form the corresponding dihydroxylated species. However, in contrast to the scenario described above where the dihydroxylated group was positioned at the end of an aliphatic chain, the dihydroxylated species in this case undergoes a dehydrogenation reaction to give a —COOH group as well as an alkyl species (i.e., R′H), as shown below [27].

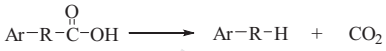




When —CH=O groups are positioned at the end of an aliphatic chain they remain active, and decomposition can occur to form carbon monoxide (CO). If the —CH=O groups react with oxygen, they form —COOH groups, as shown below [27].



The subsequent decomposition of the carboxyl group would lead to the formation of carbon dioxide (CO2), as shown below.



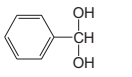
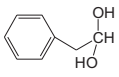
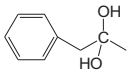
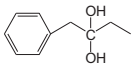
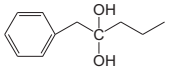
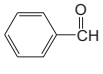
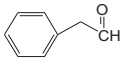
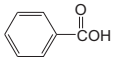
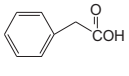
The structural and chemical characteristics of aromatic rings have been studies extensively using chemical calculation methods, and the results of these studies have indicated that the aromatic rings do not have a discernible impact on the properties of the oxygen-containing functional groups [6,9,28]. It has also been reported that there are only one or two types of aromatic ring in lignite and bituminous coal [6]. It therefore seems appropriate to replace the aromatic structures on the surface of the coal with simple phenyl groups. Based on the results described above, we have constructed molecular models of the different types of the oxygen-containing functional groups described in this paper. The details of these models are shown in Table 1.

3. Methods

3.1. Evaluation of the molecular properties

To study the heat effects resulting from the reactions of the different types of oxygen-containing functional group, we calculated the molecular properties of the different groups, including their energies and enthalpies using Density Functional Theory (DFT). The DFT calculations were conducted with a hybrid of Becke's non-local three parameter exchange using a correlation functional together with the Lee–Yang–Parr functional (B3LYP), which is gen-

Table 1
Molecular model of oxygen functional groups.

Species	Molecular model	
—OH	 R1	 R2
	 R3	 R4
	 R5	
—CH=O	 R6	 R7
—COOH	 R8	 R9

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